

SCIENCE FOR CERAMIC PRODUCTION

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ELECTROPHYSICAL PROPERTIES OF OXIDE INTERLANTHANIDES AND SOLID SOLUTIONS BASED ON THEM

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The electrophysical properties and nature of oxide interlanthanides LaYO_3 , LaYbO_3 , LaErO_3 , NdLuO_3 , LaGdO_3 , and GdLuO_3 , pure and doped by calcium and hafnium oxides with close ionic radii, are investigated within a temperature interval from 900 to 1600°C and oxygen partial pressure from 2×10^4 to 1×10^{-10} Pa. It is demonstrated that the electric conductivity of the materials considered is determined by nonstoichiometric disordering. The results obtained can be used for synthesis of new types of thermoresistors, oxygen sensors, and other ceramic sensors, as well as various dielectric materials.

Oxides of rare-earth elements (REE), due to their specific structure of $4f$ -shells, difference of ionic radii of cations, and the presence of several degrees of oxidation, offer a unique possibility for synthesis of mutual solid solutions and compounds known as oxide interlanthanides (OIL). Research on OIL is promising with respect to their electric, magnetic, optical, luminescent, and other properties.

Research on electrophysical properties of simple REE oxides revealed substantial possibilities for regulating the level and the type of electric conduction of these oxides by deviating from stoichiometry under variable partial oxygen pressure P_{O_2} and heterovalent doping [1–4].

The use of OIL substantially expands the possibilities of crystal-chemical combinations and variation of the electron structure and properties of materials. These possibilities, in particular, are related to the fact that a dopant element can act either as a donor or as an acceptor, depending on the crystal-chemical position it occupies.

In this regard, the present study investigates the electrophysical properties and type of conduction of some OIL within a wide interval of temperature and P_{O_2} : LaYO_3 ,

LaYbO_3 , LaErO_3 , NdLuO_3 , LaGdO_3 , LaHoO_3 , and GdLuO_3 , including those doped by oxides with similar ionic radii: CaO and HfO_2 . For this purpose, dense high-purity samples of the specified OIL and some solid substitution solutions based on them were synthesized (here and elsewhere molar content, unless otherwise specified): LaYbO_3 (0.5% CaO),

GdLuO_3 (0.5% CaO), GdLuO_3 (0.8% CaO), and GdLuO_3 (0.5% HfO_2).

Ternary phase diagrams of the oxides selected have not been investigated. However, it is known that the solubility of CaO in REE oxides at a temperature of 1600°C is a few percent, and that of HfO_2 is 20–25% [1, 5]. Therefore, it can be assumed that the compositions of the synthesized samples do not go beyond the limits of existence of solid solutions.

The study of the electrophysical properties was carried out within a temperature interval of 1000–1600°C in air and in media in which P_{O_2} varied within a pressure interval of 2×10^4 to 1×10^{-10} Pa using a solid-electrolyte oxygen pump.

Initial materials for synthesis of OIL were Gd_2O_3 of grade GdO-1 , Y_2O_3 — grade ItO-1 , Ho_2O_3 — grade GoO-1 , Lu_2O_3 — grade LuO-1 , La_2O_3 — grade LaO-1 , and Yb_2O_3 — grade YbO-1 , with a content of the main compound of over 99.95 wt.% [the main impurities were other REE oxides, calcium and hafnium nitrates (grade “pure for analysis”), nitric acid, and NH_4OH (grade “chemically pure”)].

The procedure of making samples included coprecipitation of hydroxides from an aqueous nitrate solution by means of an aqueous ammonium solution, their decomposition to oxides in calcination, impregnation of obtained mixtures with calcium or hafnium nitrates in the course of milling, subsequent semidry two-sided compression and high-temperature sintering in vacuum at a temperature of 1850–1900°C for 1 h, and annealing in an air medium at a temperature of 1250–1300°C for 2 h.

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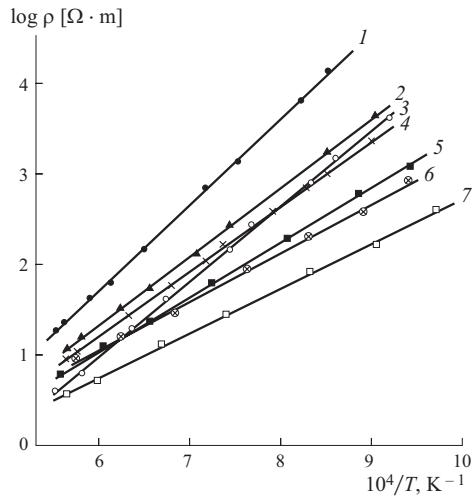


Fig. 1. Temperature dependence of the conductivity of oxide compounds and solid solutions with two rare-earth cations: 1) GdLuO_3 ; 2) LaYO_3 ; 3) LaGdO_3 ; 4) LaYbO_3 ; 5) LaHoO_3 ; 6) LaErO_3 ; 7) NdLuO_3 .

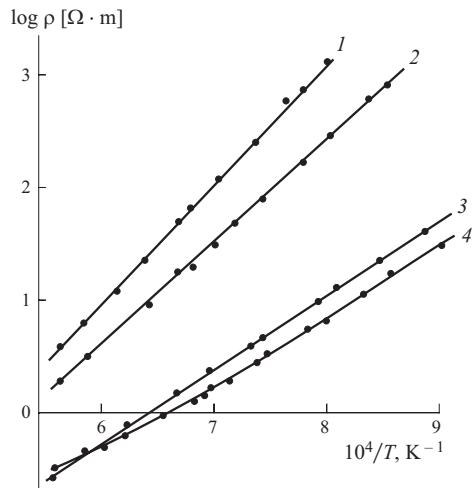


Fig. 2. Temperature dependence of the resistivity of GdLuO_3 , pure and doped with CaO and HfO_2 : 1) GdLuO_3 (0.5% HfO_2); 2) GdLuO_3 ; 3) GdLuO_3 (0.5% CaO); 4) GdLuO_3 (0.8% CaO).

The composition, microstructure, and porosity of the samples were determined by standard methods accepted in ceramic technology. Electrical conductivity was measured by the two-probe method using platinum electrons in an alternating current at a frequency of 1500 Hz according to the method described in [1]. The measurement error was not more than 10%.

The samples studied were shaped as tablets of diameter 18–20 mm and height 3–4 mm, had a homogenous microstructure, with porosity of not more than 5%, and a grain size from 20 to 80 μm (depending on the composition).

According to the data of chemical, spectral, and x-ray microprobe analysis, the chemical compositions of sintered samples correlated with estimated values, the total content of

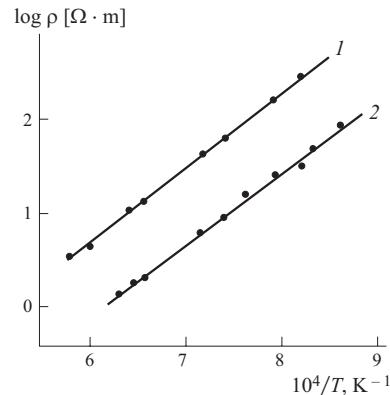


Fig. 3. Temperature dependences of the conductivity of LaYbO_3 (1) and LaYbO_3 doped with 0.5% CaO (2).

impurities did not exceed 0.15%, and the main impurities were Al and Si. There was no irregularity in the distribution of components.

X-ray and petrographic analysis indicated that all nondoped samples have one phase and either a perovskite structure of a rhombic syngony such as GdFeO_3 (LaYO_3 , LaYbO_3 , LaErO_3) or a C-shaped structure of lanthanide oxide (NdLuO_3 , LaGdO_3 , GdLuO_3). The doped synthesized samples also have one phase and represent solid substitution solutions based on the above-listed phases: LaYbO_3 (0.5% CaO), GdLuO_3 (0.5% CaO), GdLuO_3 (0.8% CaO), and GdLuO_3 (0.5% HfO_2). An exception is a sample LaYbO_3 (0.8% CaO), in which traces of a second phase are identified.

Below are the reflection indexes n of some OIL:

$1.953 > n > 1.941$ for GdLuO_3 ;

$1.939 > n > 1.932$ for GdLuO_3 (0.5% CaO);

$1.946 > n > 1.939$ for GdLuO_3 (0.5% HfO_2);

$n_g = 2.07$, $n_p = 2.0$ for LaYbO_3 ;

$n_g = 2.05 - 2.056$, $n_p = 1.99$ for LaYbO_3 (0.5% CaO).

The results of measuring temperature dependences of resistivity ρ in an air medium for the pure and doped oxides synthesized are indicated in Figs. 1–3. These dependences, as a rule, are rectilinear within a temperature interval of 1000–1600°C in coordinates $\log \rho - 1/T$, and only in the sample GdLuO_3 (0.8% CaO) are two rectilinear segments registered.

The temperature dependence ρ is used to calculate values of conduction activation energy for synthesized oxides, which are presented in Table 1.

It can be seen that the highest resistivity and conduction activation energy among the considered non-doped OIL is observed in GdLuO_3 . Doping with small quantities of heterovalent impurities significantly modifies the conductivity and conduction activation energy of OIL. For instance, the conductivity of GdLuO measured in air varies by more than two orders of magnitude at a temperature of 1000°C due to doping, and that of LaYbO_3 varies by an order of magnitude. Calcium oxide doping increases the conductivity of OIL and decreases their conduction activation energy, whereas doping

TABLE 1

Composition	Temperature interval, °C	Activation energy, eV
GdLuO ₃	1000 – 1600	1.8
GdLuO ₃ (0.5 % HfO ₂)	1000 – 1600	2.2
GdLuO ₃ (0.5 % CaO)	1000 – 1600	1.3
GdLuO ₃ (0.8 % CaO)	1000 – 1200	1.3
GdLuO ₃ (0.8 % CaO)	1200 – 1600	0.8
LaYO ₃	1000 – 1600	1.6
LaGdO ₃	1000 – 1600	1.8
LaYbO ₃	1000 – 1600	1.5
LaYbO ₃ (0.5 % CaO)	1000 – 1600	1.5
LaHoO ₃	1000 – 1600	1.2
LaErO ₃	1000 – 1600	1.1
NdLuO ₃	1000 – 1600	1.0

with hafnium oxide changes these properties in the opposite direction.

The dependences of conductivity on partial pressure of oxygen are similar for all synthesized non-doped OIL. Figure 4 shows the dependence that is typical of these materials, $\rho = f(P_{O_2})$, for NdLuO₃ for several fixed temperature levels. These dependences are usually extrapolated by the formula $\rho = \text{const } P_{O_2}^\alpha$. Thus, at $P_{O_2} > 10^2$ Pa conductivity grows as partial pressure of oxygen decreases. On this segment $\alpha \approx 0.20$. In the interval of P_{O_2} equal to $10^2 - 10^{-1}$ Pa, the isotherm slope monotonically decreases, and at $P_{O_2} < 10^{-1}$ Pa $\alpha = 0$. Within an interval of P_{O_2} of $10^{-1} - 10^{-9}$ Pa, conductivity virtually does not depend on partial pressure of oxygen. Measurements of transfer numbers using the EDS method and the thermo-ERS sign indicated that at $P_{O_2} > 10^2$ Pa hole conduction prevails for NdLuO₃, whereas at $P_{O_2} < 10^{-1}$ Pa ionic conduction prevails.

In general, the values found of α and other regularities of variation of NdLuO₃ conduction depending on the parameters considered coincide with earlier obtained data for simple oxides of REE, including those doped by analogous impurities. These results can be described within the framework of a theoretical model of equilibrium ratios between electron and ionic defects in crystals [6], whose application to the analysis of a defective structure of pure and doped REE oxides is discussed in [1].

These conclusions for REE oxides can also be extended to OIL, since the valent electronic shells of their cations are identical.

The conduction of nonstoichiometric oxides is determined by the relationship between stoichiometric and impurity defects, and the type of compensation of the charge disparity of heterovalent impurity defects varies depending on the deviation from stoichiometry in such an oxide (or on P_{O_2} of the gaseous phase, in which the measurements are performed): from compensation only by ionic defects (cation and anion vacancies, interstitial ions) to compensation only

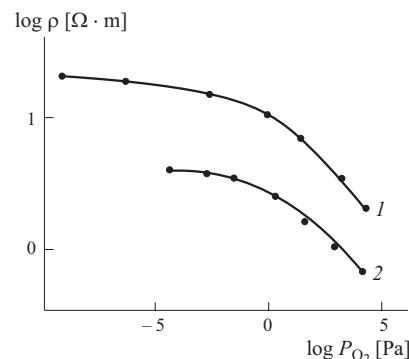


Fig. 4. Isotherms of the resistivity of NdLuO₃ depending on the partial pressure of oxygen in ambient medium at 1200°C (1) and 1350°C (2).

by electrons and conduction holes. In practice, as a rule, the intermediate case is found, where charge disparity is compensated by both types of defects, whose concentration ratio depends on the properties of the oxide and the equilibrium value of P_{O_2} in the measurements.

The specifics of OIL is related to the fact that, due to different sizes of cation, the energy of vacancy formation in these cation sublattices is unequal as well. Therefore, when oxides of heterovalent elements dissolve in OIL, the cation vacancies will be mostly arranged only in one of the cation sublattices. At the same time, due to the different structures of 4f-shells, the energy of electron defect formation related to different cations is different as well. However, it follows from the above results that these specifics do not significantly change the regularities of conductivity variation depending on temperature, doping, and equilibrium P_{O_2} .

The specifics of the defective structure observed in OIL make it possible to control conductivity and conduction activation energy within wide limits. The obtained data can be used for the synthesis of new types of thermoresistors, oxygen sensors, and other ceramic sensors, as well as diverse dielectric materials.

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